ULTRAVIOLET ABSORPTION SPECTRA OF ISOMERIC FLUOROTOLUENES IN THE LIQUID AND SOLID STATES*

S. K. Sen

Optics Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32

(*Received, February* 29, 1960)

ABSTRACT. The ultraviolet absorption spectra of isomeric fluorotoluenes in the liquid and solid states have been analysed and the results have been compared with those for the substances in the vapour state reported by previous workers.

The spectrum due to liquid state of *o*-fluorotoluene exhibits broad bands, the 0,0 band being shifted towards longer wavelengths by 238 cm^{-1} with respect to that due to vapour. The bands become sharper and shift towards shorter wavelengths when the liquid is solidified and cooled to $-180°C$.

The spectrum due to the liquid *m*-fluorotoluene appears to consist of two series of broad bands which have been assigned to monomers and dimers respectively. Only one system of bands is given by the substance in the solid state at $-180°C$. It has been shown that these results can be explained if it is assumed that all the molecules are transformed into dimers in the solid state at $-180°C$.

The spectrum due to *p*-fluorotoluene in the solid state at $-180°C$ seems to consist of two series of bands. It has been possible to analyse them on the supposition that the excited electronic energy level is split up into two components. The shift of the 0,0 band on liquefaction is observed to be larger in the case of the para compound than in the case of the ortho compound. It has therefore been concluded that the larger shift may be due to the formation of dimers even in the liquid state. The cause of the splitting has been discussed.

INTRODUCTION

Investigations on the influence of intermolecular field on the absorption spectra of some halogen substituted benzene compounds in the state of aggregation at low temperature by Swamy (1952, 1953) revealed some interesting facts. Splitting of the electronic energy level into three components was observed in the case of *o*- and *m*-chlorotoluene, *o*-dichlorobenzene and *o*-bromotoluene when the substances were solidified and cooled to $-180°C$. No splitting was, however, observed in the case of the para compounds. Similar changes in the spectra were observed later in the case of *m*-bromotoluene and *m*-dichlorobenzene by the present author (Sen, 1957). Thus, unsymmetrical disubstituted benzenes containing halogen atoms as substituents showed the splitting of the energy level.

*Communicated by Prof. S. C. Sirkar.

The electronic absorption spectra of free molecules of isomeric fluorotoluenes in the vapour state have been investigated by Cave and Thompson (1950) and the spectra of solutions of isomeric fluorotoluenes in *n*-heptane have been reported by Miller and Thompson (1949). They observed higher extinction co-efficient for *p*-fluorotoluene than in the case of *o*- and *m*-fluorotoluene.

Previous investigations on the influence of intermolecular field on the absorption spectra of halogen substituted benzenes have been confined only to compounds having either chlorine or bromine atom as a substituent. As the fluorine atom is more strongly active than the chlorine or bromine atom, it was thought worthwhile to extend the investigations to isomeric fluorotoluenes. With this object, the ultraviolet absorption spectra of *o*-, *m*- and *p*-fluorotoluene in the liquid state and in the solid state at $-180°C$ have been studied in the present investigation. The results have been discussed and compared with those for the other halogen substituted benzene compounds in the states of aggregation reported by previous workers.

EXPERIMENTAL

Chemically pure samples of *o*-, *m*- and *p*-fluorotoluene (Fisher) were distilled repeatedly under reduced pressure before being used in the present investigation.

The experimental set up was the same as in an earlier investigation by the author (Sen, 1955). Spectrograms were taken on Ilford HP3 films with Hilger El quartz spectrograph having a dispersion of 3 A.U per mm in the region of 2600 Å. Very thin films of thicknesses of the order of a few microns were required to produce the bands due to the liquid state and the time of exposure varied from 10 to 15 minutes. The corresponding spectra due to the substances in the frozen state at low temperature were recorded with a time of exposure of about 1 hr. Iron arc spectrum was taken in each spectrogram as comparison. Microphotometric records were obtained with a self-recording microphotometer of Kipp and Zonen type. The frequencies of the bands were measured using the microphotometric records of iron lines as in an earlier investigation (Sen, 1956). The slit width was 0.3 mm ($15\ cm^{-1}$) in the region of 2600 Å

RESULTS

The microphotometric records of the spectra are reproduced in Figs. 1, 2 and 3 and the wave numbers of the bands with approximate intensities and probable assignments are given in Tables I—III.

DISCUSSION

(*a*) *o-Fluorotoluene* ($C_6H_4CH_3F$) :

The absorption spectrum of *o*-fluorotoluene in the vapour state had earlier been photographed by Cave and Thompson (1950). The 0,0 band was taken at

37576 cm^{-1}. The rest of the bands were explained as due to progressions of excited state vibration frequencies 707, 924, 1230 cm^{-1} and their combinations.

They pointed out that on the longer wavelength side of the 0,0 band there is a very strong band, but they did not explain why the feebler band was taken as the 0,0 band. On examining the spectrogram reproduced by them, it is found that if the 0,0 band be identified with the strong band at 37484 cm^{-1}, two very sharp and weak bands at 37414 cm^{-1} and 37554 cm^{-1} yield a vibration frequency 70 cm^{-1} both in the ground and excited states. These two frequencies seem to be coupled with all other stronger bands giving progressions of frequencies 707 cm^{-1}, 804 cm^{-1}, 929 cm^{-1} and 1230 cm^{-1}. Also, a band giving an excited frequency 498 cm^{-1} is observed in the spectrum due to the vapour state and this band is observed in the spectrum due to crystals at $-180°C$. Hence the 0,0 band due to the vapour is fixed at 37484 cm^{-1}

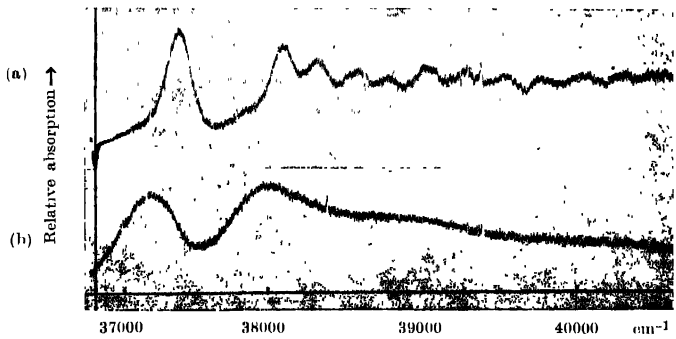

Fig. 1. Microphotometric records of the ultraviolet absorption spectra of *o*-fluorotoluene.
(a) Solid at $-180°C$. (b) Liquid at 30°C.

Four broad bands have been observed in the spectrum due to liquid state, the centre of the 0,0 band being at 37246 cm^{-1}. The 0,0 band thus shifts towards longer wavelengths by 238 cm^{-1} with liquefaction of vapour. Such a shift may be explained on the supposition that intermolecular field acting on the molecules in the liquid state lowers the excited electronic energy state. The broadness of the bands may be due to fluctuation of intermolecular field by thermal motion of molecules. The succeeding bands represent progressions of excited state vibration frequencies 707 cm^{-1} and 924 cm^{-1}, which are not different from the corresponding frequencies observed in the vapour state.

TABLE I

Absorption bands of *o*-fluorotoluene in the liquid and solid states

Vapour Cave and Thompson (1950) (Prominent bands)		Present author on the basis of spectrogram reproduced by Cave & Thompson (1950) (Prominent bands)		Liquid at 30°C.		Solid at −180°C.	
ν in cm⁻¹	Assignment	ν in cm⁻¹	Assignment	ν in cm⁻¹	Assignment	ν in cm⁻¹	Assignment
36827	0−749	37351(vw)	0−133				
37302	0−274	37414(w, very sharp)	0−70				
37576	0,0	37484(vs)	0,0	37246(s,b)	0,0	37400(vs)	0,0
38283	0+707	37554(w, very sharp)	0+70	37953(s,b)	0+707	37896(m)	0 + 496
38500	0+924	37982(w)	0+498	38170(m,b)	0+924	38107(s)	0+707
38806	0 + 1230	38121(w, very sharp)	0+707 −70	38877(w,b)	0+707+924	38324(s)	0+924
		38191(s)	0+707			38630(m)	0 + 1230
		38260(w, very sharp)	0+707+70			38815(m)	0+707×2
		38218(w, very sharp)	0 + 804−70			39035(m)	0+707+924
		38288(s)	0+804			39127(m)	0 + 496 + 1230
		38358(w, very sharp)	0+804+70			39250(m)	0 + 924×2
		38413(s)	0+929			39552(m)	0 + 924+1230
		38714(m)	0+1230			39741(m)	0+707×2+924
						40044(m)	0+707×2+1230
						40261(w)	0+707+924+1230

On solidification and cooling of the substance to −180°C, the spectrum yields a sharper system of bands with the 0,0 band at 37400 cm⁻¹ shifted by 154 cm⁻¹ towards shorter wavelengths with respect to its position in the liquid state. Progressions of excited state vibration frequencies 496, 707, 924, 1230 cm⁻¹ have been observed. As mentioned earlier, the frequency 496 cm⁻¹ also appears in the vapour state and it may correspond to the ground state vibration frequency 530 cm⁻¹. *o*-Fluorotoluene does not seem to exhibit any splitting of electronic energy level unlike orthochloro- and orthobromotoluene.

(*b*) *m-Fluorotoluene* ($C_6H_4CH_3F$)

The ultraviolet absorption spectrum due to vapour state of *m*-fluorotoluene was analysed by Cave and Thompson (1950). They found a large number of feeble bands within a distance of 240 cm^{-1} from the 0,0 band at 37398 cm^{-1} on the shorter wavelength side and a set of strong bands on the longer wavelength side. The latter bands were assigned to $v \rightarrow 0$ transitions with ground state vibration frequencies 70, 184, 253, 311, 520 and 726 cm^{-1}.

In the liquid state the first band appears to consist of two unresolved broad bands with centres at 36965 cm^{-1} and 37212 cm^{-1}. The next two prominent bands have a separation of 685 cm^{-1} from the first two bands respectively. The succeeding bands are very broad having no structure.

TABLE II

Absorption bands of *m*-fluorotoluene in the liquid and solid states

Vapour (Cave & Thompson (1950) (Prominent bands)		Liquid at 30°C		Solid at −180°C.	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
36935	0 − 1003				
36672	0 − 726				
36878	0 − 520				
37087	0 − 311				
37145	0 − 184 − 70				
37176	0 − 253				
37214	0 − 184				
37243					
37273	0 − 70				
37325					
37346					
37368					
37398	0,0	36965 (s)	A_0	37239 (s)	0,0
37486	0 + 684 − 520	37212 (s)	B_0	37924 (s)	0 + 685
37496	− 70				
		37650 (s)	A_0 + 685	38163 (s)	0 + 924
37535					
		37896 (s)	B_0 + 685	38485 (s)	0 + 1246
37558	0 + 684 − 520				
37573				38853 (m)	0 + 685 + 924
37631	0 + 965 − 726			39087 (m)	0 + 924 × 2
37680	0 + 282			39412 (m)	0 + 924 + 1246
37892	0 + 457			39733 (w)	0 + 1246 × 2
38082	0 + 684			40331 (w)	0 + 924 × 2 + 1246
38363	0 + 965				
38659	0 + 1261				

The spectrum seems to consist of two series of bands separated by 247 cm^{-1} and one of these series seems to disappear with solidification of the liquid. Hence it has been assumed that the two series are produced respectively by the monomers and dimers present in the liquid and that in the solid state at $-180°C$, all the molecules are transformed into dimers.

When the liquid is solidified and cooled to $-180°C$, the first band becomes narrower and appears to consist of only one broad band with its centre at 37239 cm^{-1}. However, the 0,0 band due to the frozen mass at $-180°C$ is not sharp but it has a width of about 100 cm^{-1}. This cannot be due to the presence of unresolved bands due to $0 \rightarrow v$ transitions by the side of the 0,0 band on the shorter wavelength side because the first band is quite symmetrical throughout the whole width, and similarly, all the succeeding bands on the short wavelength side are equally wide. It appears, therefore, that these widths of the bands are due to perturbation produced by neighbouring molecules in the cyrstal on the electronic energy level of the molecule. This perturbation being small, there is no observable splitting into three components as observed in other cases of halogen substituted meta compounds It appears from Fig. 2(a) and Table II, that in the spec-

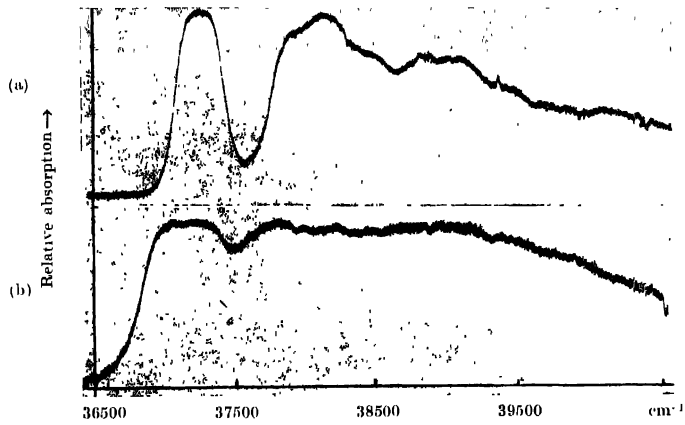

Fig. 2. Microphotometric records of the ultraviolet absorption spectra of *m*-fluorotoluene.
(a) Solid at $-180°C$. (b) Liquid at 30°C.

trum due to solidified *m*-fluortoluene at $-180°C$, there are bands due to vibrational transitions of excited state frequencies 685, 924 and 1246 cm^{-1}. While the first frequency remains unaltered with change of state, the latter two correspond to the frequencies 965 and 1261 cm^{-1} observed in the vapour state. The fact that the first band due to solid state at $-180°C$ is displaced towards shorter wavelengths from the position of the first band due to the liquid state confirms the assignment

indicated above, because generally with solidification and cooling of the crystals to −180°C, the 0,0 band shifts towards shorter wavelengths, In the present case the 0,0 band at 36965 cm^{-1} due to the dimers shifts towards shorter wavelengths with solidification of the liquid

The assignment of the bands on both sides of the 0,0 band due to vapour state made by Cave and Thompson (1950) is confirmed by the fact that these bands disappear at low temperature.

(*c*) *p-Fluorotoluene* ($C_6H_4CH_3F$)

The analysis of the spectrum due to para compound in the vapour state made by Cave and Thompson (1950) shows the 0,0 band to be at 36876 cm^{-1} and the succeeding bands are assigned to progressions of excited state frequencies 185, 398, 584, 794, 843, 1014, 1194 and 1229 cm^{-1}. In the liquid state broad bands have been observed with the 0,0 band at 36517 cm^{-1}. Thus, there is a shift of the 0,0 band by 359 cm^{-1} towards longer wavelengths on liquefaction of vapour. The succeeding bands represent transitions corresponding to vibrational frequencies 843 and 1230 cm^{-1} not different from the corresponding frequencies observed for the vapour state.

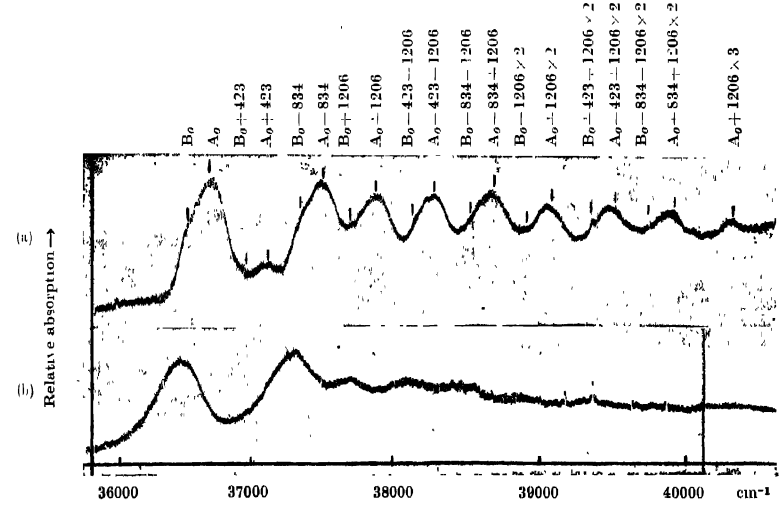

Fig. 3. Microphotometric records of the ultraviolet absorption spectra of *p*-fluorotoluene.

(a) Solid at −180°C. (b) Liquid at 30°C.

It is evident from Fig. 3(a) and Table III that in the spectrum due to solid state at −180°C, each strong band is accompanied by a weaker one on the longer wavelength side. The first weak band cannot be due to a $v \rightarrow 0$ transition, because the corresponding band due to $0 \rightarrow v$ transition is absent. Hence, it is concluded that there is a splitting of the bands in the solid state. The distance between the components is observed to be 188 cm^{-1} and assignments of the bands have been made on the assumption that the excited electronic energy level is split up into two components with a separation of 188 cm^{-1}.

The excited state vibrational frequencies are observed to be 423, 834 and 1206 cm^{-1}. The new excited state frequency 423 cm^{-1} does not seem to have been observed in the vapour state and the other two frequencies may correspond to the frequencies 843 cm^{-1} and 1229 cm^{-1} observed in the spectrum due to the vapour. The intense component of the 0,0 band is shifted towards shorter wavelengths by 223 cm^{-1}.

A comparison of the spectra due to the vapours of the ortho- and para dichlorobenzene shows that the 0,0 band shifts to longer wave lengths by about 450 cm^{-1} with the change from the ortho to the para configuration. In the present case a similar shift of about 608 cm^{-1} is observed with the change from ortho to the para position of the fluorine atom. When the vapour is liquefied the 0,0 band again shifts towards longer wavelengths by about 359 cm^{-1} while in the case of the ortho compound the shift with liquefaction of vapour is only 238 cm^{-1}. Hence this larger shift in the case of the para compound may be due to formation of dimers in the liquid state.

In the case of *o*-chlorotoluene, *o*- dichlorobenzene and *m*-dichlorobenzene (Swamy, 1952, 1953, Sen, 1957) each band was found to be split up into three components, the central component being the strongest. In the spectra of *m*-chlorotoluene (Swamy, 1952), *o*-bromotoluene (Swamy, 1953) and *m*-bromotoluene (Sen, 1957) in the solid state the strongest of the three components is on the short wavelength side of the other two components. In the case of *p*-fluorotoluene also, the weaker component is on the longer wavelength side of the stronger component in each of the bands.

It has already been pointed out by Sirkar and Misra (1959) that the so called Davydov splitting is not observed in the case of certain crystals owing probably to the fact that the contribution of only a few neighbours predominates in the interaction of transition moments of neighbouring molecules on the energy of any particular molecule, and therefore,the oscillator strength determined with a large number of molecules in the absorbing path cannot be used in this case. They also pointed out that when the transition takes place in the field of the permanent dipoles surrounding any molecule in the crystal there may be a splitting of the bands. Probably in the case of *p*-fluorotoluene also, the splitting is due to the interaction of such dipoles on the electronic transition in the molecule.

TABLE III

Absorption bands of *p*-fluorotoluene in the liquid and solid states

Vapour Cavo & Thompson (1950) (Prominent bands)		Liquid at 30°C.		Solid at ~ 180°C	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
35720	0 − 1156				
36632	0 − 844				
36051	0 − 825				
36235	0 − 641				
36423	0 − 453				
36539	0 − 337				
36565	0 − 311				
36659	0 − 217				
36780	0 − 96				
36831	0 − 40			36552 (w)	B_0
36876	0,0	36517 (s,b)	0,0	36740 (s)	A_0
36906	0 + 185 − 96	37360 (s,b)	0 + 843	36975 (w)	B_0 + 423
37001	0 + 584 − 453	37747 (m,b)	0 + 1230	37163 (m)	A_0 + 423
37061	0 + 185	38200 (m,b)	0 + 843 × 2	37386 (m)	B_0 + 834
37175	0 + 398 − 96	38591 (w,b)	0 + 843 + 1230	37568 (s)	A_0 + 834
37218	0 + 398 − 40	39435 (w,b)	0 + 843 × 2 + 1230	37758 (w)	B_0 + 1206
37231				37948 (s)	A_0 + 1206
37274	0 + 398			38185 (w)	B_0 + 423 + 1206
37460	0 + 584			38368 (s)	A_0 + 423 + 1206
37670	0 + 794			38598 (w)	B_0 + 834 + 1206
	0 + 398 × 2			38778 (s)	A_0 + 834 + 1206
37719	0 + 843			38968 (w)	B_0 + 1206 × 2
37890	0 + 1014			39157 (s)	A_0 + 1206 × 2
38070	0 + 1194			39389 (w)	B_0 + 423 + 1206 × 2
38105	0 + 1229			39576 (s)	A_0 + 423 + 1206 × 2
				39796 (w)	B_0 + 834 + 1206 × 2
				39989 (s)	A_0 + 834 + 1206 × 2
				40359 (m)	A_0 + 1206 × 3

188

ACKNOWLEDGMENT

The author is indebted to Professor S. C. Sirkar, D.Sc., F.N.I., for his kind interest and constant guidance throughout the progress of the work.

REFERENCES

Cavo, W. T. and Thompson, H. W., 1950, Discussions Faraday Society, 9, 41.
Miller, C. H. and Thompson, H. W., 1949, *J. Chem. Phys.*, **17**, 845-6.
Sen, S. K., 1955, *Ind. J. Phys.*, **29**, 561.
„ 1956, *Ind. J. Phys.*, **30**, 56.
„ 1957, *Ind. J. Phys.*, **31**, 99.
Sirkar, S. C. and Misra, T. N., 1959, *Ind. J. Phys.*, **33**. 45-50.
Swamy, H. N., 1952c, *Ind. J. Phys.*, **26**, 445.
„ 1953a, *Ind. J. Phys.*, **27**, 55.
„ 1953b, *Ind. J. Phys.*, **27**, 119.